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Assessment of Ethylene Dichloride as a Potential Air Pollution Problem. Volume III

GCA Corp, Bedford, Mass GCA Technology Div

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ASSESSMENT OF ETHYLENE DICHLORIDE AS A POTENTIAL AIR POLLUTION PROBLEM

VOLUME III

FINAL REPORT

Contract No. 68-02-1337

Task Order No. 8

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U.S. ENVIRONMENTAL PROTECTION AGENCY

Research Triangle Park

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Volume II	Methyl Alcohol	Volume IX	Methyl Methacrylate
Volume III	Ethylene Dichloride	Volume X	Ortho-Xylene
Volume IV	Benzene	Volume XI	Maleic Anhydride
Volume V	Acetone	Volume XII	Dimethyl Terephthalate
Volume VI	Acrylonitrile	Volume XIII	Adipic Acid
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ASSESSMENT OF ETHYLENE DICHLORIDE AS A POTENTIAL AIR POLLUTION PROBLEM

Volume III

by

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ABSTRACT

This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

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Volume XIV	Phthalic Anhydride.

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SECTION I

SUMMARY AND CONCLUSIONS

Ethylene dichloride (EDC) is a clear, colorless oily liquid with a pleasant chloroform-like sweet odor and taste. Industrially it is made from ethylene by direct chlorination or by oxychlorination. EDC is used as an industrial solvent in cleaning and extraction processes. It is also used as a fumigant and as a lead scavenger in gasoline. However, most EDC produced goes into the manufacture of vinyl chloride monomer.

Data correlating acute or chronic ethylene dichloride (EDC) exposures to human response are quite limited. Depending on the exposure time, acute EDC poisoning may occur at high concentrations (above 3000 ppm) through attack on the central nervous system. The current OSHA standard for worker exposure to EDC is a time weighted average of 50 ppm for an 8-hour work day, 40-hour work week. Chronic exposure to sufficiently high concentrations of EDC may cause loss of weight, drowsiness, vomiting, and nervousness. EDC has been used as a grain and seed fumigant and does not affect seed germination. The hydrogen-carbon bonds in EDC are reactive, and decomposition occurs in the troposphere. Thus, it does not seem to pose a direct threat to stratospheric ozone.

Emissions of EDC are primarily a result of EDC production, end product manufacture, solvent usage, and bulk storage and transportation. Total emissions of EDC are estimated to be 163 million lb/year. EDC production and end product manufacture are the two largest sources, accounting for 36 and 52 percent respectively of total emissions. Estimated 1974 production was 9300 million pounds by 14 plants with about 86 percent produced

in Texas and Louisiana. Production is expected to increase at 9 percent per year through 1978. EDC is used primarily (77 percent) to manufacture vinyl chloride monomer.

Emissions of EDC may be controlled by several methods. Currently only scrubbers and condensers are used to control EDC emissions from manufacturing processes. Incineration is a third technique; however, hydrochloric acid and chlorine gas are produced during incineration. Fixed roof storage tanks can be controlled by venting to a condenser, or they can be converted to a floating roof design.

Simple diffusion modeling estimates place the likely maximum 1-hour average ambient concentration outside the work environment at about 5 ppm. The maximum 24-hour average ambient concentration might be expected to be about 3 ppm.

Based on the results of the health research presented in this report, and the ambient concentration estimates, it appears that ethylene dichloride as an air pollutant does not pose a threat to the health of the general population. In addition, ethylene dichloride does not appear to pose other environmental insults which would warrant further investigation or restriction of its use at the present time. However, two actions should be considered: (1) that concentrations be monitored in a small-scale program around one of the larger EDC production facilities or vinyl chloride monomer production facilities, and (2) that potential adverse effects on the earth's ozone layer be monitored in conjunction with the research into the effects of other halocarbons.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Ethylene dichloride (EDC) is a clear, colorless oily liquid with a pleasant chloroform-like sweet odor and taste. Industrially it is made from ethylene by direct chlorination or by oxychlorination. EDC is used as an industrial solvent in cleaning and extraction processes. It is also used as a fumigant and as a lead scavenger in gasoline. However, most EDC produced goes into the manufacture of vinyl chloride monomer.[1] Selected physical and chemical properties are presented in Table 1.

Table 1. SIGNIFICANT PROPERTIES OF EDC

Synonyms: 1,2 - dichloroethane; sym. - dichloroethane; ethylidene chloride	
Chemical formula	CH_2 Cl CH_2 Cl
Molecular weight	98.97
Boiling point	83.5°C
Melting point	-35.3°C
Specific gravity	1.253 (20°/4°C)
Vapor density	3.34 (air = 1)
Vapor pressure	62 mm Hg at 20°C
Solubility	0.9 parts/100 parts of water at 0°C soluble in ethanol and ether
Explosive limits	6.2 percent to 15.9 percent by volume
Auto ignition temperature	413°C
Flash point	13°C (closed cup)
At 25°C and 760 mm Hg	1 ppm vapor = 3.97 mg/m^3 1 mg/m^3 vapor = 0.252 ppm

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - Reports in the literature correlating the concentration of ethylene dichloride in air with acute human response are lacking. At high concentrations in air, probably approaching 1000-3000 ppm based on studies done on animals, EDC is irritating to the eyes, nose, and throat. Two men exposed to 1200 ppm EDC vapor for 2 minutes experienced little discomfort, except that the odor of EDC was extremely noticeable.[2] Halogenated hydrocarbons such as EDC, upon inhalation, typically cause general stupor, mental confusion, dizziness, nausea, vomiting, symptoms of central nervous system depression and gastrointestinal upset.[3,4] It is possible to recover from such symptoms with no after effects.

Only a few fatal cases of acute EDC poisoning have been reported. In one case a workman repairing a vessel used to transport EDC became unconscious after exposure for only a few minutes.[5] He appeared to recover, but several hours later lapsed into a coma and died. His skin was covered by an oily mass due to the separation of carotene in the skin, caused by skin absorption of EDC. However, absorption through the skin is too small to be significant in contributing to systemic poisoning. There was considerable pulmonary edema, liver degeneration, renal congestion, and meningeal hemorrhages. In a second case, two men exposed to a leaking EDC pipe for 30 minutes died hours later with suppression of urine production, jaundice, and circulatory failure.[6] However, the primary target of EDC after inhalation appears to be the central nervous system.

Oral ingestion of 1 to 2 ounces, about 845 mg/kg body weight,[7] of EDC by an adult male is fatal.[8,9] Body reaction to the dose may be delayed as much as 2 hours, with death occurring up to 22 hours later. The autopsy report after the ingestion of 1 ounce of EDC showed hemorrhage damage in the stomach, lungs, and brain, with acute toxic kidney degeneration and diffuse pathological death of liver cells.

Chronic Poisoning - Chronic exposure of man to EDC has not been well documented. Two cases were reported in a cholesterol producing plant where EDC was used as a solvent.[10] One worker, employed for 9 weeks, complained of weight loss, drowsiness, and nervousness. The other subject, employed for 5 months, complained of upper-abdominal pain and tremor of the tongue. Both complained of nausea and vomiting. After removal from the vapors, all symptoms disappeared.

The odor of EDC is barely detectable at 50 ppm, and is not unpleasant in the 100 to 200 ppm range.[5] The odor of EDC is not sharp enough to act as a warning of dangerous chronic exposure, according to inhalation studies done on animals. Based primarily on animal exposure data, the NIOSH recommended standard for exposure to EDC is a 50 ppm time weighted average over an 8-hour shift.[7] The individual may be exposed to 100 ppm for a maximum of 10 minutes, but never above 200 ppm.

Effects on Animals

Acute Poisoning - The symptoms in animals of acute EDC exposure are similar to human symptoms. Table 2 shows the correlation between EDC dose and duration of exposure to symptoms produced in guinea pigs. The period of recovery from semi-consciousness and unconsciousness to the normal actions of guinea pigs varied from 15 to 60 minutes. However, depending on the concentration and time of exposure, many of the apparently recovered animals died within 8 days. The principal pathological findings after death were congestion and edema of the lungs, and kidney degeneration. No serious internal damage was found in guinea pigs exposed to 60,000 ppm for 5 minutes, 17,000 ppm for 10 minutes, 4,000 ppm for 30 minutes, 2,000 ppm for 120 minutes, and 1,100 ppm for 480 minutes.

Table 2. CORRELATION OF SYMPTOMS, EXPOSURE TIME AND CONCENTRATION FOR GUINEA PIGS INHALING EDC[2]

Symptom	Concentration, ppm				
	2,000	4,000-4,500	10,000-17,000	25,000-35,000	60,000-70,000
Nose and eye irritation	6[a]	3-10	1-2	1-2	1
Unsteadiness	20-45	8-18	2-3	1-2	1-2
Inability to walk	(480)	30	4-10	3-5	2-4
Retching	(480)	(360)	7-15	5-13	2-4
Jerky, rapid respiration	(480)	(360)	10-30	5-13	4-8
Unconsciousness	(480)	30-60	10-20	4-7	3-7

[a]Time of exposure in minutes. Values in parentheses indicate the time of exposure where the stated symptoms were not observed.

Table 3 summarizes mortality in seven species of animals due to a single exposure to EDC. Note that in many cases death after exposure to EDC did not occur for several days. Twenty young adult rats showed responses to the 7-hour exposure varying from mild stupor to complete loss of consciousness. The rats were alive at the end of the exposure period, but all died within 48 hours. Microscopic tissue examination revealed congestion of the viscera, particularly of the liver and spleen, fatty degeneration of the liver, and kidney degeneration.

Exposure of dogs to 1000 ppm for 7 hours produced a clouding of the cornea that was reversible.[4] After repeated exposures, the dogs became resistant to the clouding. This effect has not been demonstrated in man. Subcutaneous injection of EDC (1 cc/kg body weight) into rats produced an average mortality rate of 35 percent in 24 hours, with a high incidence of fatty changes in heart, liver, and kidney.[12]

Chronic Poisoning - Table 4 summarizes the mortality rates for the types of animals exposed to 1500 ppm EDC for 7 hours per day. After the

Table 3. MORTALITY AFTER SINGLE EXPOSURES TO EDC[11]

Animal	Number	Weight, grams	Time, hours	Mortality Ratio	Cumulative mortality, days after exposure					
					0	1	2	3	4	5
Exposure, 3000 ppm										
Rabbits	16	3,940	7	12/16	0	7	11	12		
Guinea pigs	14	885	7	14/14	0	11	13	14		
Hogs	2	27,300	7	2/2	0	0	2			
Cats	3	3,240	7	0/3						
Raccoons	2		7	0/2						
Mice	22		7	22/22	22					
Mice	19		2	19/19	0	19				
Rats	20	146	7	20/20	0	19	20			
Rats	16	177	3½	15/16	0	1	3	5	13	15
Rats	15	257	1½	0/15						
Exposure, 1500 ppm										
Guinea pigs	12	321	7	6/12	0	1	4	5	6	
Mice	20		7	20/20	4	20				
Mice	23		2	1/23	0	0	0	1		
Rats	20	170	7	4/20	0	2	2	4		
Rats	13	257	4	0/13						

Table 4. MORTALITY OF ANIMALS EXPOSED TO 1500 ppm EDC[11]

Animal	Number	Weight, grams	Mortality	Total deaths					
				Number of exposure days					
				1	2	3	4	5	6
Rats	29	125	29/29	0	5	17	26	29	
Rabbits	5	1,640	4/5	1	1	1	2	4	
Guinea pigs	9	250	9/9	1	6	8	9		
Dogs	3		2/3	0	0	0	0	1	2
Hogs	2	32,300	2/2	1	2				

first exposure, walking became difficult, there was a loss of appetite, and bloody crusts appeared around the nose. After three exposures the animals lay on their sides with very shallow breathing, and moved with difficulty. Autopsy revealed hemorrhage of the adrenal gland, hemorrhage and congestion of the lungs, and kidney tubule degeneration.

Autopsy results for the five animal types were similar. Exposures to lower concentrations for longer periods were also evaluated. At 1000 ppm,[11] repeated 7-hour exposures were rapidly fatal to guinea pigs, rats, and mice. Dogs, cats and monkeys survived a period of 23 to 55 days. At 400 ppm and repeated 7-hour exposures, dogs remained in good health for 8 months, while rabbits were only able to survive 100 exposures. At 200 ppm, deaths still occurred among guinea pigs and rats after 126 exposures. In another study[4] guinea pigs and rats survived for 212 days while being exposed to 200 ppm EDC, 7 hours per day, 5 days per week, but half the pigs showed histological changes.

Rats, guinea pigs, rabbits, and monkeys, exposed to a lower concentration of 100 ppm, survived for 168 days with no ill effects.[5] Rats, guinea pigs, and rabbits tolerated 100 ppm for a 17-week period, with exposure for 6 hours per day, 5 days per week.[13]

The chronic toxicity of EDC in mice can be linked to its metabolic breakdown. EDC breakdown appears to involve the enzymatic removal of one its chlorine atoms, resulting in the formation of chloroacetate.[14,15] The toxicity of chloroacetate has been ascribed to the lability of the chlorine, by which the compound can react with the thiol groups of proteins, disrupting normal protein function and structure.[15]

Effects on Vegetation

EDC is widely used as a grain and seed fumigant, and thus would not inhibit the germination of any sprayed seeds. (See below.)

Other Effects

Effects of Use - In the past, EDC has been widely used as an insecticidal fumigant, both as a pure compound and mixed with 25 percent carbon tetrachloride, according to a 1928 report.[5] For years the Dow Chemical Company has manufactured a series of Dowfume fumigants[17] as listed below.

	Weight percent		
Fumigant	Ethylene dichloride	Carbon tetrachloride	Ethylene dibromide
Dowfume 75	70.2	29.8	--
Dowfume EB-5	29.2	63.6	7.2
Dowfume EB-15	19.6	60.0	20.4

Dowfume 75 has essentially the same acute oral and vapor toxicity as EDC. Dowfume 75 and EB-5 are used in the control of insects in stored grain and animal feed, while EB-15 is used as a fumigant for mill machinery. In a recent study zero or trace amounts of EDC were found as residues in bread made from EB-5 fumigated grain.[18]

Effects of Decomposition - Typical chlorocarbon decomposition products are phosgene, chlorine, and hydrogen chloride, all noxious to man. Welding tests in the presence of 500 ppm EDC produced only small amounts of chlorine and hydrogen chloride. The possibility exists that when the compound is burned or heated at higher concentrations, the noxious decomposition products could be significant.[19,20]

Effects on Ozone - Evidence[21,22] demonstrates that the photocatalyzed removal of chlorine atoms from chlorofluorocarbons results in a catalytic chain reaction destroying ozone in the stratosphere. However, halogenated compounds such as EDC containing relatively reactive hydrogen-carbon bonds are more likely to be destroyed by attack from atmospheric OH

radicals before reaching the upper atmosphere. EDC does not present a threat to the ozone layer due to a short lifetime in the atmosphere with decomposition at lower levels.

AMBIENT CONCENTRATIONS AND MEASUREMENT

Ambient Concentration Estimates

The greatest emission source of ethylene dichloride is a vinyl chloride manufacturing plant, located in a town of about 2000 population, with a capacity of up to 1000 million pounds/year. Assuming a 1 percent loss of ethylene dichloride based on vinyl chloride production, this amounts to 10 million pounds/year of ethylene dichloride emissions. As a more useful emission rate for ambient concentration estimation, this converts to:

$$\frac{(10 \times 10^6 \text{ lb/yr})\ (453.6 \text{ g/lb})}{3.1536 \times 10^7 \text{ sec/yr}} = 143.8 \text{ g/sec.}$$

Some assumptions must be made regarding this ethylene dichloride release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations within the plant where ethylene dichloride vapor leaks or is vented to the atmosphere. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed.

Ground level concentrations can then be estimated at locations downwind of the facility.[23] To do this a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100m/4.3 = 23.3m.$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z} \; e^{-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2}$$

or

$$\chi = \frac{143.8}{(2)\pi(36)(18.5)} \; e^{-\frac{1}{2}\left(\frac{10}{18.5}\right)^2}$$

$$= 2.969 \times 10^{-2} \; g/m^3$$

for a 10-minute average concentration. Over a period of an hour this becomes:

$$(2.969 \times 10^{-2} \; g/m^3) \; (0.72) = 2.138 \times 10^{-2} \; g/m^3$$

or 5.4 ppm 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about 3 ppm.

Measurement Technology

Two sample collection techniques are used in air sampling for ethylene dichloride. These are collection in aqueous pyridine solution in a bubbler or impinger, and collection on silica gel. Analysis of samples

collected by the first technique is achieved by colorimetric methods, whereas gas chromatography is used to analyze samples collected on silica gel.

Using the bubbler or impinger collection method, concentrations as low as 25 ppm may be determined from a 1-liter gas sample. The sample is heated in a water bath followed by cooling and addition of sodium hydroxide. Ethyl alcohol is used to dilute the sample before reading the optical density at a wavelength of 415 mμ with a spectrophotometer. Carbon tetrachloride, chloroform, trichloroethylene and ethylene chlorohydrin do not interfere with the analysis but chlorine (at 3 ppm) does interfere. This method may not be sensitive enough for measuring atmospheric concentrations.

In the second method the sample is collected by silica gel in a narrow glass tube. The sample is desorbed from the silica gel by heating and passed through a gas chromatograph. Similar compounds have been measured by using a Celite 545 column and a flame ionization detector.[24]

SOURCES OF ETHYLENE DICHLORIDE EMISSIONS

Ethylene Dichloride Production and Consumption

The production of ethylene dichloride (EDC) is estimated to have been 9300 million pounds in 1974 and is expected to increase at 9 percent per year through 1978.[25] Approximately 77 percent of all ethylene dichloride produced is used to manufacture vinyl chloride monomer. Presently, almost all production is carried on by large plants producing a balanced combination of ethylene dichloride and vinyl chloride. The consumption of ethylene dichloride for final products and the expected growth rate for each product are shown in Table 5.

Table 5. ETHYLENE DICHLORIDE CONSUMPTION - 1974[26]

Product	Millions of pounds	Expected annual growth rate
Vinyl chloride	7,141	9%
Exports	791	steady
Lead scavenger	280	decline in use
Trichloroethylene	260	decline in use
Perchloroethylene	245	6%
Methyl chloroform	210	9%
Ethyleneamines	184	7%
Vinylidene chloride	175	7%
Miscellaneous	14	7%
Total	9,300	9%

Ethylene dichloride is manufactured by 10 companies at 14 locations. About 50 percent is produced in Louisiana and 36 percent is produced in Texas. The largest plant represents 18 percent of total EDC production capacity. A list of EDC producers including their production capacity and plant location is presented in Appendix A. Because the majority of EDC is used to produce vinyl chloride monomer, a list of vinyl chloride monomer producers is presented in Table 6.

Ethylene Dichloride Sources and Emission Estimates

Ethylene dichloride emissions result from end product manufacturing, ethylene dichloride production, miscellaneous solvent uses, and bulk storage and distribution. Total emissions from all categories are estimated to be 163 million pounds representing 1.8 percent of total production (see Table 7).

Table 6. VINYL CHLORIDE MONOMER PRODUCERS USING PYROLYSIS OF EDC - 1974[28]

Company	Location	Capacity, million lb/yr
Allied Chemical	Baton Rouge, La.	300
American Chemical	Long Beach, Cal.	165-170
Continental Oil	Lake Charles, La.	600
Dow Chemical	Freeport, Texas	180
	Plaquemine, La.	300-340
	Oyster Creek, Texas	800
Ethyl Corporation	Baton Rouge, La.	270
	Pasadena, Texas	150
B.F. Goodrich	Calvert City, Ky.	875-1000
PPG Industries	Lake Charles, La.	300
	Guayanilla, P.R.	500-575
Shell Chemical	Deer Park, Texas	700
Total[a]		5,140-5,385

[a]An additional 525-550 million pounds are produced by hydrochlorination of acetylene.

Table 7. ETHYLENE DICHLORIDE EMISSIONS - 1974

Source	Emissions, million lb/yr
End product manufacturing	85
Ethylene dichloride production	58
Solvent usage	14
Bulk storage and distribution	6
Total	163

The major source of ethylene dichloride emissions is the manufacturing of end products, primarily vinyl chloride. Based on a 1 percent loss, emissions from this category are 85 million pounds.[27]

The second major source is the manufacturing of ethylene dichloride. EDC is produced chiefly by two processes, direct chlorination of ethylene and oxychlorination as outlined below:

Direct chlorination: $CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2\ CH_2Cl$

ethylene — chlorine — ethylene dichloride

Oxychlorination: $2\ CH_2 = CH_2 + O_2 + 4HCl \rightarrow 2\ ClCH_2\ CH_2Cl + 2\ H_2O$

ethylene — oxygen — hydrochloric acid — ethylene dichloride — water

Emissions from the direct chlorination process are relatively small compared to the oxychlorination process. Specifically, atmospheric pollutants from the direct chlorination process are less than 1/5 of those emitted by the oxychlorination method for the same quantity of product.[28]

The main sources of emissions from the oxychlorination process are the process vent stream and the fractionation vent stream. Estimated average emissions from these sources are 986 lb/hr of ethylene dichloride for a 700 million lb/yr plant.[28] Based on these data and the 1974 production of ethylene dichloride by the oxychlorination process (42 percent of 9300 million lb), emissions of EDC from this manufacturing process are 48.2 million lb/yr. Total ethylene dichloride emissions from both manufacturing methods are, therefore, estimated to be 58 million lb/yr.

The third major source of EDC emissions is the use of EDC as a solvent. It is assumed that the total quantity of material used for this purpose is lost to the atmosphere. Solvent usage is estimated to be 14 million pounds.[26]

The last major source of emissions is the storage and distribution of EDC. In present plants fixed roof tanks are used and are vented to the atmosphere because the vapor pressure is low (3 psi at 100°F). It is estimated that EDC emissions from storage and handling are 6 million lb/yr based on a 0.06 percent loss factor.[28]

ETHYLENE DICHLORIDE EMISSION CONTROL METHODS

Emissions of EDC may be controlled by several methods. Currently only scrubbers and condensers are used to control EDC emissions from manufacturing processes.[29] Incineration may also be used but formation of HCl and Cl_2 might create an emission problem. Fixed roof storage tanks can be vented to a condenser or converted to a floating roof design.

Scrubbers and Condensers

Scrubbers are employed primarily to remove small amounts of HCl and in some cases chlorine left in the noncondensed reactor effluent. A water scrubber is able to remove most of the HCl, but dilute caustic is required to eliminate all of the chlorine from the vent gas. Depending on the operating conditions some EDC may also be absorbed (39 percent).[29]

The second control device currently being used by the industry is the condenser. This system, unlike the aqueous scrubber, is designed primarily to recover EDC. The recovery of 97.9 percent of EDC is reported by the industry when the effluent stream is cooled to -10°F.[29]

Cost data for both systems are presented in Table 8. While the capital cost for condensers is almost four times higher than scrubbers, the condenser system has a higher recovery of EDC resulting in an overall net savings. The overall hydrocarbon control efficiency is also greater (89.4 percent compared to 25 percent).

Table 8. COST DATA[a] FOR SCRUBBERS AND CONDENSERS FOR CONTROL OF EDC EMISSIONS[29]

	Scrubber	Condenser
Gas rate, lb/hr	65	178
Installed cost material and labor, $	12,300	207,200
Annual operating cost, $	3,520	22,700
Value of recovered product, $/yr (credit)	1,800	(87,400)
Annual net operating cost, $ (credit)	1,720	(64,700)
Overall hydrocarbon control efficiency	25%	89.4%
EDC control efficiency	39%	97.9%

[a] Costs updated to 1st quarter 1975.

Incineration

Several combustion devices have been proposed for the control of emissions of EDC and other chlorinated compounds resulting from the manufacture of EDC. However, none of these systems, which are mentioned below with their related costs, are currently being used by the industry. The primary objection to their use is the formation of HCl and Cl during combustion, which must be scrubbed out of the effluent stream.

Table 9 presents cost data for four systems:

1. Direct fired boiler and caustic scrubber
2. Thermal incinerator and caustic scrubber
3. Thermal incinerator and waste heat boiler with a caustic scrubber
4. Flare system.

Table 9. COST DATA[a] FOR THE CONTROL OF ETHYLENE DICHLORIDE BY INCINERATION[28]

	Direct fired boiler and caustic scrubber	Thermal incinerator and caustic scrubber	Thermal incinerator, waste heat boiler, and caustic scrubber	Flare system
Total flow, lb/hr	78,588	78,588	78,588	17,588
SCFM	17,280	17,280	17,280	17,280
Total capital cost, $	1,600,000	800,000	1,096,000	141,000
Operating cost, $/yr	819,000	538,000	652,000	414,000
Steam production, $ (savings)	(234,000)	-	(234,000)	-
Recovered EDC, $ (savings)	-	-	-	-
Net annual cost, $	585,000	538,000	418,000	414,000
Percent control of EDC	≈100%	≈100%	≈100%	-

[a]Costs updated to 1st quarter 1975.

Storage Tanks

Control of emissions from storage tanks would require the use of floating roof tanks or condensers. Emissions from fixed roof tanks can readily be vented to the condensers previously described without any significant increase in cost. If a condenser system is not readily available, the fixed roof tanks could be converted to floating roof tanks. A 70 percent reduction in emissions can be achieved by conversion. Figure 1 provides estimated costs of various gasoline storage tanks.[30] These equipment cost estimates can also be applied to EDC. As can be seen, conversion of fixed roof to floating roof tanks by installation of internal floating covers is more economical than the installation of new pontoon floating roof tanks.

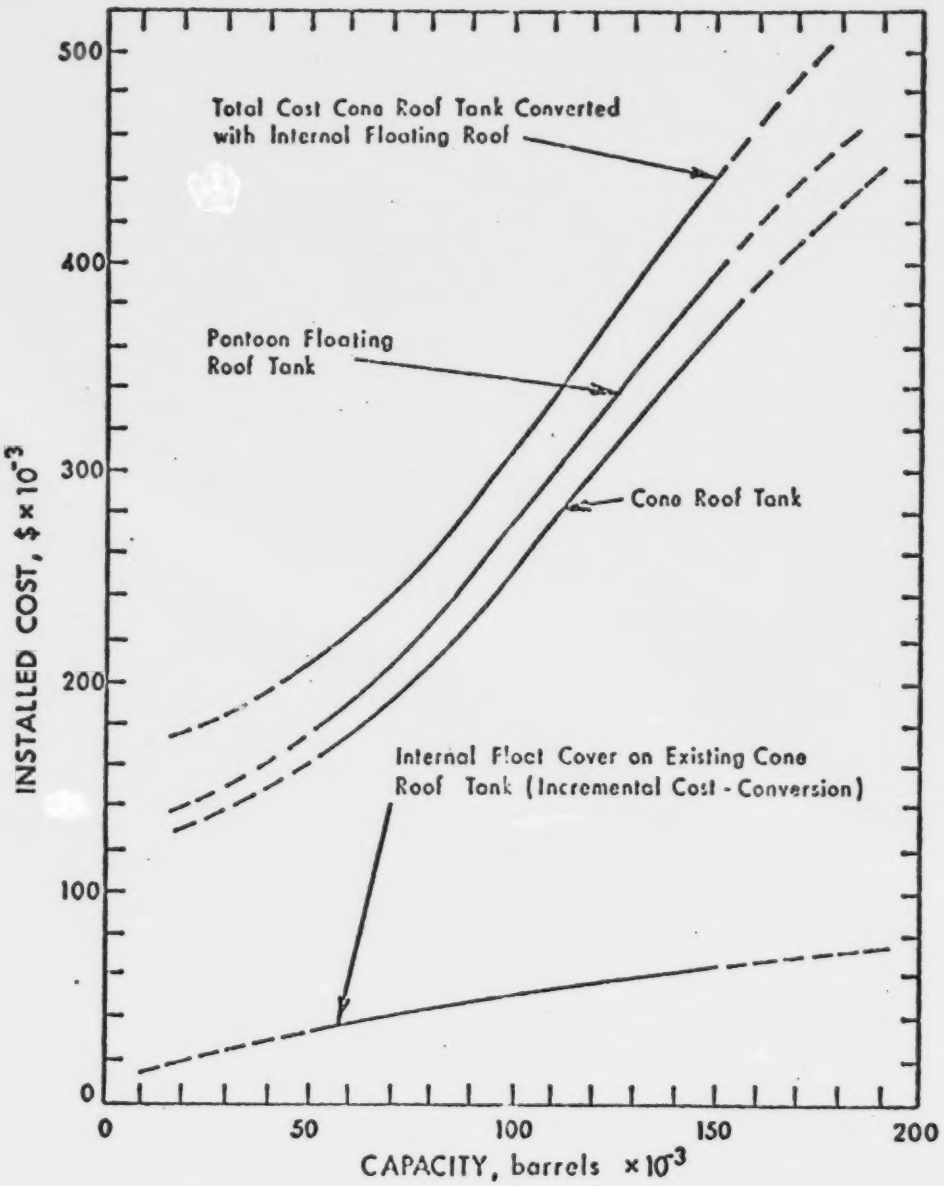

Figure 1. Estimated installed cost of EDC storage tanks (equipment costs assumed to be the same as gasoline storage tanks)[30]

SECTION III

REFERENCES

1. Kent, J. A. (Ed). Riegel's Handbook of Industrial Chemistry, Seventh Edition. New York, Van Nostrand Reinhold Company, 1974.

2. Sayers, R. R., W. P. Kant, F. A. Patty. Acute Response of Guinea Pigs to Vapors of Some New Commercial Organic Compounds: I. Ethylene Dichloride. Public Health Reports, U.S. Reprint No. 1949, January 31, 1930.

3. Stevens, H. Neu otoxicity of Some Common Halogenated Hydrocarbons. In: Laboratory Diagnosis of Diseases Caused by Toxic Agents. Sunderman, F. W., and F. W. Sunderman, Jr. (ed). St. Louis, Warren H. Green, Inc., 1970. p. 193-194.

4. Irish, D. C. Halogenated Hydrocarbons. I. Aliphatic-Ethylene Dichloride. In: Industrial Hygiene and Toxicology, Second Revised Edition, Patty, F. A. (ed). New York, Interscience Publishers, 2:1280-84. 1962.

5. Browning, E. Toxicity and Metabolism of Industrial Solvents. Amsterdam, Elsevier Publishing Co., 1965. p. 247-52.

6. Brass, K. Fatal Dichloroethane Poisoning. Deut Med Worchschr. 74: 553, 1949. Cited in: Industrial Toxicology, Second Edition, Fairhall, L. T. New York, Hafner Publishing Co., 1969. p. 213-214.

7. The Toxic Substances List 1974 Edition. U.S. Department of Health Education and Welfare Publication No. (NIOSH) 74:134.

8. Hueper, W. C., C. Smith. Fatal Ethylene Dichloride Poisoning. Am J M Sci. 189:778, 1935. Cited in: Ethylene Dichloride Poisoning. McNally, W. D., Fostvedt, G. Ind Med. 10:373-74, 1941.

9. Lochhead, H. B., H. P. Close. Ethylene Dichloride Plastic Cement: A Case of Fatal Poisoning. J Amer Med Assoc. 146:1323, 1951.

10. McNally, W. H. and G. Fostvedt. Ethylene Dichloride Poisoning. Ind Med. 10:373-74, 1941.

11. Heppel, L. A., P. A. Neal, T. L. Ferrin, K. M. Endicott, V. T. Porterfield. The Toxicology of 1,2-Dichloroethane (Ethylene). J Pharm Exp Ther. 84:53-63, 1945.

12. Highman, B., L. A. Heppel, R. J. Lamprey. The Toxicology of 1,2-Dichloroethane (Ethylene Dichloride). Arch Path. 51:346-50, 1951.

13. Hoffman, H. Th., H. Birnstiel, P. Jobst. On the Inhalation Toxicity of 1,1- and 1,2-Dichloroethane. Arch Toxicol. 27:248-65, 1971.

14. Yllner, S. Metabolism of 1,2-Dichloroethane -^{14}C in the Mouse. Acta Pharmacol et Toxicol. 30:257-65, 1971.

15. Heppel, L. A., V. T. Porterfield. Enzymatic Dehalogenation of Certain Brominated and Chlorinated Compounds. J Biol Chem. 176:763-69, 1946.

16. Yllner, S. Metabolism of Chloroacetate-1-^{14}C in the Mouse. Acta Pharmacol et Toxicol. 30:69-80, 1971.

17. McCollister, D. C., M. S. Hollingsworth, F. Oyen, V. K. Rowe. Comparative Inhalation Toxicity of Fumigant Mixtures. Arch Ind Health 13:1-7, 1956.

18. Berck, B. Fumigant Residues of Carbon Tetrachloride, Ethylene Dichloride, and Ethylene Dibromide in Wheat, Flour, Bran, Middlings, and Bread. J Agr Food Chem. 22:977-84, 1974.

19. Rinzema, L. C., L. G. Silverstein. Hazards from Chlorinated Hydrocarbon Decomposition During Welding. Amer Ind Hyg Assoc J. 33: 35-40, 1972.

20. Noweir, M., E. A. Pfitzer, T. F. Hatch. Decomposition of Chlorinated Hydrocarbons: A Review. Amer Ind Hyg Assoc J. 33:454-59, 1972.

21. Scientists Detail Chlorofluorocarbon Research. Chem Eng News. 53:21-23, 1975.

22. Rowland, S. Aerosol Sprays and the Ozone Shield. New Sci. 64:717-720, 1974. Also in: Fluorocarbons-Impact on Health and Environment. Hearings Before the Subcommittee on Public Health and Environment of the Committee on Interstate and Foreign Commerce, House of Representatives, Serial No. 93-110, December 11-12, 1974, p. 22-25.

23. Turner, D. Bruce. Workbook of Atmospheric Dispersion Estimates. U.S. Environmental Protection Agency Report AP-26. January 1973.

24. Cropper, F. R., and S. Kaminsky. Determination of Toxic Organic Compounds in Admixture in the Atmosphere by Gas Chromatography. Anal Chem. 35:735, 1963.

25. Chemical Profiles. Schnell Publishing Co. 1974.

26. Chemical Economics Handbook. Stanford Research Institute, Menlo Park, California, 1972.

27. Survey Reports on Atmospheric Emissions from the Petrochemical Industry. Vinyl Chloride Via EDC Pyrolysis. Volume IV. U.S. Environmental Protection Agency. Publication No. EPA-450/3-73-005-d. April 1974.

28. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Volume 3: Ethylene Dichloride Manufacture by Oxychlorination. U.S. Environmental Protection Agency. Publication No. EPA-450/3-73-006-c. November 1974.

29. Survey Reports on Atmospheric Emissions from the Petrochemical Industry. Ethylene Dichloride (Direct). Volume II. U. S. Environmental Protection Agency. Publication No. EPA-450/3-73-005-b. April 1974.

30. Hydrocarbon Pollutant Systems Study. MSA Research Corp. NTIS Publication No. PB-219-073. October 1972.

APPENDIX A

ETHYLENE DICHLORIDE PRODUCERS - 1974[29]

		Total capacity, million lb/yr	Direct chlorination, million lb/yr	Oxychlorination, million lb/yr
Allied Chemical Corporation	Baton Rouge, La.	645	430	215
American Chemical Company	Long Beach, Calif.	325	225	100
Conoco Chemicals	Lake Charles, La.	968	476	492
Diamond Shamrock Chemical Co.	Deer Park, Texas	265	95	170
Dow Chemical Company	Freeport, Texas	1,100	628	472
Dow Chemical Company	Plaquemine, La.	1,160*	600	560
Ethyl Corporation	Baton Rouge, La.	550	290	260
Ethyl Corporation	Houston, Texas	260	260	
The B. F. Goodrich Company	Calvert City, Ky.	990	330	660
PPG Industries, Inc.	Lake Charles, La.	1,040	803	237
Shell Chemical Company	Deer Park, Texas	1,700	1,126	574
Union Carbide Corporation	Taft, La.	150	150	
Union Carbide Corporation	Texas City, Texas	150	150	330
Vulcan Materials Company	Geismar, La.	330		330
Total		9,633	5,563	4,070

*Oxychlorination facility presently not in operation.